In the analysis of Samples 1 and 2 the solutions had to be filtered to remove suspended organic matter in order to permit titration with permanganate, yet no trouble was encountered in titrating with dichromate without filtration. Samples 3–6 inclusive did not contain organic matter. All of these results are average results of closely agreeing duplicating analyses.

Conclusions.

1. The concentration of acid should be small when titrating small amounts of iron with dichromate, using ferricyanide as indicator on the spot plate. If the concentration is quite large ferric chloride should be added to give a sharper color change on the spot plate.

2. Boric acid counteracts the influence of hydrofluoric acid in the dichromate titration of ferrous iron and hence addition of this reagent to the hydrofluoric acid extraction of the silicate yields a solution in which the ferrous iron can be accurately titrated with dichromate, using ferricyanide as indicator on a spot plate.

MADISON, WISCONSIN.

NOTE.

Use of Acetone for Drying Chemical Utensils.—Acetone is miscible in all proportions with water. It has a boiling point of 56°. On account of these two properties acetone is an excellent substance to use as a wash to facilitate the drying of glassware, especially flasks, bottles, etc. After cleaning and rinsing with water the vessel is allowed to drain a short time, then sufficient acetone is added to give a good wash. After again draining a few seconds the remaining acetone is removed by drawing air through the vessel by inserting a glass tube which is connected to suction, or by the application of heat. The author has found the use of acetone very serviceable, replacing the use of alcohol to remove the water, then ether to remove the alcohol. The acetone has the merit of being cheaper than either alcohol or ether at the present time. O. L. BARNEBEY.

UNIVERSITY OF WISCONSIN, MADISON.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SOUTH DAKOTA.]

DERIVATIVES OF PHENYL ETHER.

BY ALFRED N. COOK AND FRANK F. SHERWOOD.

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2-Nitro-4′-methyl phenyl ether ($NO_2.C_6H_4OC_6H_4.CH_3$) was first prepared by one of the authors[1] of this paper about sixteen years ago and some of its derivatives were prepared and studied. Subsequently some other compounds of an analogous nature and corresponding derivatives

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[1] *Am. Chem. J.*, **24**, 525–529 (1900).

were prepared and described. Since the first paper was not as comprehensive as those that appeared subsequently, it was thought that a further study of the above-mentioned compound would be of some interest and profit.

The method here used was somewhat varied and shortened in the light of subsequent experience and as a consequence the yield was somewhat increased. *o*-Bromo-nitro benzene, with somewhat more than the theoretical equivalent of potassium cresolate, was warmed on an oil bath to 125° until all action had ceased. The temperature was then gradually raised to 160°. The potassium cresolate employed was also prepared somewhat differently than in the first instance, with the result that a much whiter and better product was obtained, which was probably one factor in the increased yield. No water was added to the mixture of potassium hydroxide and *p*-cresol. The two substances were simply mixed and then heated on the water bath until as dry as possible. The drying was then completed in the air bath at about 110° for a short time. Care must be exercised in the final heating, since, if the heat is applied too long, the substance begins to char and the final product is not so good.

The nitro-methyl phenyl ether was purified by fractional distillation *in vacuo* several times and subsequent crystallization from alcohol. In spite of the fact that an excess of potassium phenolate was always employed in its preparation there always remained behind some unchanged nitro-bromo benzene to contaminate the product. Apparently also there was always some by-product formed which, however, was not studied. The above method of purification was found to be much better and more expedient than the one formerly employed. The compound boiled at 210° under a pressure of 15 mm. and melted at 49°, the same as first[1] determined.

A hexa-nitro-methyl phenyl ether ($(NO_2)_6.CH_3.C_{12}H_3$) was obtained by treating the mother substance with concentrated nitric acid at the temperature of the boiling water bath. The reaction takes place very slowly and it is necessary to heat for some time before solution takes place. The acid solution was poured into a large amount of water, when the nitro-compound was precipitated as a viscous mass, which, on stirring for several minutes, completely solidified. It is very soluble in hot alcohol and but sparingly soluble in cold alcohol. It is soluble in benzene, ether, carbon disulfide and sparingly soluble in water. After crystallization from alcohol several times it melted at 103.5°.

Analyses for nitrogen yielded 18.13% and 18.22%, respectively. Theory, 18.55%.

On account of the small yield obtained it was thought that a part of the substance might have remained behind in the acid solution. On greatly diluting the solution, however, no further precipitation took place,

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[1] *Loc. cit.*

but on neutralizing the acid solution with caustic soda a second crop of crystals separated out on standing, which were of a higher degree of purity than the first crop. A considerable portion of the substance remained behind in solution in the water, since the substance is slightly soluble in water. A hexa-nitro compound was prepared by the senior author of this paper some years ago[1] by nitrating 4-nitro-4′-methyl phenyl ether in an analogous manner. Its melting point was not determined, but its other properties are identical with those of this compound. With little doubt I think the two compounds are identical.

Bromo-2-nitro-4′-methyl phenyl ether ($Br.NO_2.CH_3.C_{12}H_7O$) was prepared by dissolving 2-nitro-4′-methyl phenyl ether in carbon disulfide, adding a small crystal of iodine to act as a catalytic agent or carrier for the bromine, and then a large excess of bromine and allowing to stand two or three days. After evaporating off the carbon disulfide and distilling under diminished pressure, the compound was purified by crystallizing from alcohol several times, when it melted at 23°. It is a yellow-colored substance, very much resembling the mother substance from which it was prepared.

Two analyses for bromine yielded 34.18% and 34.3%, respectively. Theory requires 34.6%.

Bromo-2-amino-4′-methyl phenyl ether ($Br.NH_2.CH_3.C_{12}H_7O$) was obtained by reducing the bromine derivative of the mother substance with tin and hydrochloric acid in alcoholic solution while warming on the water bath and subsequent separation of the tin with hydrogen sulfide and evaporating to crystallization. The compound is quite stable and yields a *free base* with caustic alkalies which is likewise quite stable. With platinic chloride it yields a *chloroplatinate* which crystallizes in brilliant reddish crystalline grains.

Platinum found, 20.22%. Theory requires 20.00%.

2-Nitro-4′-methyl phenyl ether sulfonic acid ($NO_2.CH_3.C_{12}H_7.SO_3H$) was prepared by precipitating the lead of the lead salt with hydrogen sulfide and evaporating to crystallization. It is of a yellow color and fumes in the air when warmed on the water bath even when dissolved in considerable water. On bringing the open mouth of a bottle containing ammonium hydroxide near the warmed acid dense, white clouds are formed similar to those formed by ammonia and hydrochloric acid. When aspirated with a current of air in water solution, or in the dry state into a second tube containing distilled water for a couple of hours, sufficient acid passed over to yield a test with litmus and affect the sense of taste. Of the various salts prepared none were found to contain any water of crystallization. This acid, therefore, differs from all of the other analogous acids so far prepared, since one or more of the salts of all of the other sul-

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[1] THIS JOURNAL, **25**, 64 (1903).

fonic acids contain from one to several molecules of water of crystallization. The acid causes various carbonates to effervesce. The composition of this acid is sufficiently shown by the analysis of several of its salts.

2-Amino-4′-methyl phenyl ether sulfonic acid ($NH_2.CH_4.C_{12}H_7.SO_3H$) was prepared by reducing the corresponding copper salt of the sulfonic acid in water solution with tin and hydrochloric acid while warming on the water bath, removing the tin by means of hydrogen sulfide, and evaporating to crystallization. Although it is both base and acid it possesses fairly pronounced acid properties. It causes the effervescence of carbonates.

Lead-2-nitro-4′-methyl phenyl ether carbonate was prepared by dissolving the mother substance in a small quantity of sulfuric acid containing a small quantity of sulfur trioxide, adding to a large amount of water, treating with lead carbonate until effervescence ceases, filtering and evaporating to crystallization. The lead salt thus prepared seemed to be quite difficult to purify and persisted in giving abnormally high results for lead for a long time.

Pb found after repeated crystallization, 25.2%. Theory, 25.15%.

The barium salt was prepared in an analogous manner as in the case of the lead salt with the substitution of barium carbonate. It is of a slightly yellow color, very soluble in hot water and but slightly so in cold water, and comparatively easy to purify. It contains no water of crystallization. It crystallized in radial aggregations so characteristic of the compounds of phenyl ether so far prepared.

Barium found, 15.4%. Theory, 15.15%.

The strontium salt was prepared similarly to the barium and lead salts with the substitution of strontium carbonate. It is of a light yellow color and contains no water of crystallization.

Found 12.29% and 12.18% of strontium, respectively. Theory, 12.45%.

The copper salt was prepared by adding the calculated amount of copper sulfate to the barium salt to completely precipitate the barium and evaporating to crystallization. It is quite sparingly soluble in water, from which it crystallizes on cooling in a very bulky mass. When moist the salt is of a nearly white color, with perhaps a slight yellow tinge; when dry, however, it possesses a slight greenish tinge. It readily reduces with tin and hydrochloric acid and yields a stable, free base.

The cadmium salt was prepared in the same general manner as the copper salt with the substitution of cadmium sulfate. It is of a yellowish white color, and fairly soluble in water, from which it crystallizes in bulky, radial aggregations. It contains no water of crystallization.

The sodium salt was prepared by precipitating the barium of the barium salt by means of sodium carbonate and evaporating to crystallization. It is of a light yellow color and very soluble in water.

Sulfur found, 9.64% and 9.75%, respectively. Theory, 9.66%.

The compound seemed to be very hard to oxidize, even for a sulfur compound, requiring two full days' heating with fuming nitric acid under pressure at a high heat.

2-Nitro-4′-methyl phenyl ether sulfonchloride ($NO_2.CH_3.C_{12}H_7.SO_2Cl$) was prepared by treating the sodium sulfonate with an excess of phosphorus pentachloride. The two substances were powdered, mixed thoroughly, shaken to insure complete mixing, when an action took place accompanied by a marked rise of temperature, the mixture assuming a semi-pasty condition. Ice water was then poured into the flask and allowed to remain several hours with occasional shaking. The sulfonchloride remained in the bottom of the flask in the form of solid granules and was separated by filtration with suction. The substance is very stable towards water and alcohol. The substance is soluble in alcohol, benzene, and other organic solvents. It crystallizes from alcohol in light yellow plates which melt at 69° (uncor.).

VERMILLION, S. DAK.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

PHENOLS III. THE PREPARATION OF SOME NEW SUBSTITUTED CRESOLS.[1]

BY ARTHUR J. HILL AND LOUIS E. GRAF.

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The work recorded in this paper is a continuation of an investigation on phenols and related compounds which was begun by Johnson and Hodge[2] in 1913. It is the third paper on this subject and is devoted to the synthesis and description of some new derivatives of *p*-cresol.

Our knowledge regarding the alkyl derivatives of the three isomeric cresols is somewhat limited. While several have been described in the literature, in many cases, however, the position occupied by the substituent alkyl group is held as uncertain.

Only two propyl cresols have been described. One of these, 2-hydroxy-4-propyl-1-methylbenzene, was synthesized by Bayrac,[3] who obtained it by alkali fusion of 1-methyl-4-propyl-benzenesulfonic acid. The other, 3-hydroxy-?-normal propyl-1-methylbenzene, was prepared by Mazzara[4]

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[1] The experimental work described in this paper was done by Mr. Louis E. Graf in candidacy for the Degree of Master of Science in the Sheffield Scientific School of Yale University.

[2] THIS JOURNAL, **35**, 1014 (1913).

[3] *Bull. soc. chim.*, [3] **13**, 896 (1895).

[4] *Gazz. chim. ital.*, **12**, 167 (1882).